CERTIFICATION OF APPROVAL

Separation of Moisture from Natural Gas Using Membrane Separation

By

Alia Najiah Alias

A project Dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirements for the
BACHELOR ENGINEERING (Hons.)
(CHEMICAL ENGINEERING)

Approved by,

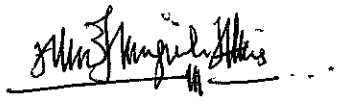
(Dr. Hilmi Mukhtar)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK DARUL RIDZUAN
JUNE, 2004

t
TP
159
.A398
2004
1. Membrane separatio
2. ChE -- Thesis

CERTIFICATION OF ORIGINALITY

This is certify that I am responsible for the work submitted in this project, that the original work I as my own except as specified in the references and acknowledgements, and that original work contained herein have not been undertaken or done by unspecified sources or persons.



(ALIA NAJIAH ALIAS)

ABSTRACT

Natural gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, most useful of all energy sources and gives many uses to the residentially, industrially and commercially. The natural gas has to be treated in several processing steps especially dehydration and hydrocarbon dew point in order to meet the required pipeline and quality specifications. The impurities especially water has to be removed in order to avoid the build-up of gas hydrates and to upgrade the gas pipeline specifications. For this study, membrane technology is the main concern as it is now becoming a new technology and one of the alternatives in gas separation beside the existence technology such as adsorption or cryogenic distillation process.

The method used in carrying out this research project is through modeling using MathCAD software. The scope study is determination on the permeability of the pure methane and moisture, and the mixture of methane and moisture with respect to the changed in parameters such as pressure, temperature and pore size. The study is extended to analyze the selectivity (separation factor) of both gases with respect to pressure, temperature and pore size complete mixing model.

Throughout the study, it could be concluded that the permeability is most favorable at higher pore size, temperature, pressure and moisture contents. The separation of moisture from the methane is most enhanced at the higher pressure and pore size but at lower temperature. By using the selected membrane with pores size equals to 0.4 nm, ξ=0.272 and τ=0.3676, the separation is proved to occur through the mathematical modeling using MathCAD. The results obtained are satisfied and fulfilled all the objectives of this study.

ACKNOWLEDGEMENT

First and for most, I would like to take this opportunity to express my thanks to all the individuals who directly or indirectly involved in completing this Final Year Research Project (FYP) through semester January 2004.

The acknowledgements with appreciations are given to my supervisor, Dr. Hilmi Mukhtar for his guidance and valuable comments through out the completion of the project. Thanks are extended to the coordinators of the FYP; Pn. Anis Suhaila Shuib and Miss Yuliana Yuhana for their support and commitment to schedule and organize all the activities in systematically.

My thanks also go to my colleague, Muhammad Kamal Kamaruzzaman for his opinions and suggestion in the discussion of this study.

Finally, sincere gratitude to others not listed here for the encouragement, support and giving the great opinion.

Thank you.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS AND NOMENCLATURE

q_f	Total feed flowrate	$[mol.s^{-1}]$
q_o	Outlet reject flowrate	$[mol.s^{-1}]$
q_p	Outlet permeate flowrate	$[mol.s^{-1}]$
A_m	Membrane area	$[m^2]$
P'_A	Permeability in the membrane	$[mol.s.kg^{-1}]$
t	Membrane thickness	[m]
p_h	Total pressure at high pressure-side	$[kg.m^{-1}.s^{-2}]$
p_l	Total pressure at low pressure-side	$[kg.m^{-1}.s^{-2}]$
x_o	Mole fraction at reject stream	[-]
y_p	Mole fraction at permeate stream	[-]
x_f	Mole fraction at feed stream	[-]
α^*	Ideal separation factor	[-]
D_{Ai}	Normal diffusion of species A into species I in mixed gas	$[m^2.s^{-1}]$
D_i	Normal diffusion of species i	$[m^2.s^{-1}]$
D_s	Surface diffusion	$[m^2.s^{-1}]$
f	Equilibrium loading factor	$[m^3.kg^{-1}]$
P	Permeability	$[mol.s^{-1}][m][m^{-2}][kg^{-1}.m.s]$
M	Molecular weight	[m]

P	Average pressure in the membrane pore	$[kg.m^{-1}.s^{-2}]$
P_{Ci}	Critical pressure of species i	$[kg.m^{-1}.s^{-2}]$
P_r	Pressure ration between permeate and feed side	$[kg.m^{-1}.s^{-2}]$
r_g	Gas radius	[m]
r_p	Pore radius	[m]
T	Temperature	[K]
T_{Ci}	Critical Temperature of species i	[K]
t_m	Membrane thickness	[m]
x_i	Fraction of species i	[-]
x_j	Fraction of species j	[-]
z	Compressibility factor	[-]
λ	Mean free path	[m]
τ	Tortuosity	[-]
μ	Viscosity	$[kg.m^{-1}.s^{-1}]$
μ_{mix}	Viscosity of mixture	$[kg.m^{-1}.s^{-1}]$
ξ	Porosity	[-]
ρ_m	Membrane density	$[kg.m^{-3}]$
Σv	Volume diffusion of atom and structure	[-]
ΔH_{ads}	Difference of heat adsorption	$[kg.m^{-2}.s^{-2}.kgmol^{-1}]$

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, most useful of all energy sources and gives many uses to the residentially, industrially and commercially. It is combustible gases, and when burned it gives off a great deal of energy. The natural gas produced at the well head has to be treated in several processing steps especially dehydration and hydrocarbon dew point in order to meet the required pipeline and quality specifications. The impurities especially moisture has to be removed in order to avoid the build-up of gas hydrates.

Table 1.1: Typical composition of natural gas that meets the specification of PGB pipelines

Compositions	Formula	Typical Analysis (%)	Range (%)
Methane	CH_4	93.56	87-96
Ethane	C_2H_6	1.78	1.8-5.1
Propane	C_3H_8	0.01	0.1-1.5
Carbon Dioxide	CO_2	0.7	0.1-1.0
Nitrogen	N_2	1.6	1.3-5.6
Oxygen	O_2	0.02	0.01-0.1
Hydrogen	H_2	Trace	Trace
Moisture	H_2O	Trace	Trace

Table 1.0 shows the typical composition of natural gas taken from PETRONAS Gas Berhad (PGB) that meets the PGB pipeline specifications (refer Appendices).

The natural gas coming from the well contents impurities that need to undergo a purification process and have to meet the pipeline specification (refer to Table 1.0). For this study, membrane technology was chosen as it is now becoming an alternatives method in removing the impurities instead of the adsorption or cryogenic distillation. Both existence technology are high capital investment and perhaps need more expert to operate it. The membrane-based technology for the gas separation become one of the most exciting and significant new unit processes, and has gained a huge importance technology.

Since 1980s, applications of gas permeation through dense polymeric membranes have increased dramatically, include (1) separation of hydrogen from methane; (2) adjustment H_2-to-CO ratio in synthesis gas; (3) O_2 enrichment in air; (4) N_2 enrichment of air; (5) drying of natural gas and air. Natural gas can be transferred directly through a pipeline or stored it as a liquid. Many natural gas distributors store liquefied natural gas in order to meet peak demands. Somehow, before natural gas can be liquefied, impurities such as moisture and CO_2 must be removed to prevent freeze up. Although amine solutions will remove CO_2 and alumina will remove moisture, using molecular sieves to adsorb both impurities at the same time is more cost-effective.

1.1 PROBLEM STATEMENT

1.2.1 Problem Identification

The commonly used technology such as adsorption has shortcomings with respect to the environmental aspects, energy consumption, and weight and space requirements. This technology which particularly need a regeneration process has the disadvantage of needing time for a bed to acquire the regeneration temperature. The regeneration temperature needs to be controlled to an appropriate temperature so that no hot spot or incomplete regeneration will develop. Furthermore, at high temperature may affect the product and accelerate ageing processes in the adsorbent (Coulson & Richardson, 1991), and will cause pores to coalesce and capacity to reduce. If too low a regeneration temperature, may result incomplete regeneration. Thus, the effluent concentration is subsequent adsorption stages will be higher than its design value. The most industry uses this technology as it is able to produce high purity for low concentration stream and can remove trace component in bulk stream. Furthermore, the combination with membrane technology can enhance the quality of pipeline gas.

The cryogenic as well is the existence technology used in removing the impurities in natural gas. The technology is capable to produce high purity natural gas and can combine with liquefaction process for producing liquid natural for export. Somehow, the technology requires high energy consumption and pre-treatment process to remove mercury. The operation is complex and difficult for the operator to operate and with the existence of the moving part, it is high operational cost.

The alternative in gas separation was carried over using membrane technology which already applies since 1980s (Seader, 1998). A gas separation membrane preferentially removes one or more components of gas mixture that is passed across a membrane surface. The fact that no mechanical and chemical processes are

involved makes the membrane process simple and easy to operate. In spite of the market and technical obstacles, gas separation membrane processes have penetrated a wide variety of markets and applications. This penetration is due to the inherent advantages of these membranes in applications, as it is environmental friendly and avoids further pollution. Furthermore, using this membrane technology is more reliable and favorable due to the low capital investment (low cost especially for small sizes), ease of operation, low energy consumption, low labor intensity, low maintenance (no moving parts), the modular design permitting easy expansion or operation at partial capacity and as well as safety factors.

However, even there are as many as advantages in using membrane technology, it still has a limitation. According to Seader, 1998, for high temperature applications, where polymer cannot be used. The membrane such as glass, carbon and inorganic oxides are available in market, but are limited in their selectivity. Thus, generally, it cannot withstand at high temperature. A product purities are economically limited, as example for air separation; retentate of 95-99% N_2 and permeate of 30-45%, thus, it is the production of nitrogen rather than oxygen.

1.2.2 Significant of the project

Membrane technology for the separation of water vapor from the natural gas is considered as a new technology. The technology is extension to the membrane for separation of liquid/liquid and liquid/solid such as reverse osmosis, ultrafiltration and microfiltration. The significant of this project is to observe the performance and the efficiency of the membrane for the water vapor removal from natural gas. Through out this project, the research study is carried out on the permeability with respect to the operating parameters such as temperature, pressure and pore size for the pure water, pure methane and the mixture of both components. The following section of this study is to perform a study on the separation factor between CH_4 and moisture.

1.2 OBJECTIVE AND SCOPE OF STUDY

1.2.1 The relevance of the project

The relevance of this project is to model through mathematical equation using MathCAD software on the removal of moisture from natural gas through membrane separation process.

The objectives of this research project are:

a) To develop a simulation models for predicting the performance of membrane for the dehydration of natural gas using PEBAX inorganic membrane separation.
b) To study the permeability of the moisture, methane and the mixture of moisture and methane with respect to varying the parameters such as temperature, pressure, pore size, and moisture feed concentration, and consider the three mechanisms takes place; Knudsen diffusion, surface diffusion and viscous diffusion.
c) To study the selectivity/separation factor when varying the temperature, pressure and pore size.

1.2.1 Feasibility of the Project within the Scope and Time Frame

The research project schedule is illustrated in Table A1 at the Appendix1, which clearly exhibited the individual milestone for Semester Jan 2004. Based on the table, the time frame in completing this project has been divided equally and feasibility for the whole semester.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 THE CRITICAL CONSIDERATIONS IN REMOVING MOISTURE IN NATURAL GAS

Moisture is one of the impurities and contaminated present in natural gas. Even though the concentration of the moisture in natural gas is traceable and very low, it is able to provide a higher effect to the pipeline specifications and it lowers the quality of natural gas. Thus, the natural gas must be upgraded by removing the moisture and other impurities content, by going through the purification process. For this case study, the separation technology concerned is through the membrane process and becoming one of the alternatives technologies instead of adsorption and cryogenic distillation.

The present of moisture can detract from the heating value and properties of natural gas that directly will lower the quality of natural gas. The hydration of natural gas is concerned as for preventing the hydrate formation. The hydrate formation is the crystallization (form 'snow') of the reaction between the moisture (free water vapor) and any hydrocarbon that smaller than normal butane. The hydrate composition contents of 6 volumes of methane molecules to 1 molecules of moisture. The study was done by Durham, 1999, analyzed that the condition normally happened as the natural gas pipeline with a moisture content 7 lbs/mmscf is compressed to 3600 psig, it has a dew point of 52 °F/11°C, and when compressed natural gas is subjected to temperatures below the 52 °F/11°C, the moisture begins to condense. If the temperature falls below 32 °F/0°C, the moisture will freeze and form the crystal. The

crystal will create a blockage (chocking) at the pipeline especially at the elbow of the pipe.

When the moisture in the natural gas mixed with the other impurities especially H_2S and CO_2, the reaction will form a corrosive mixture that will destroys the equipment and pipeline. The corrosive pipeline at the metal surface will content other contaminants and slowly will initiate a crack at the surface of the metal. Under a higher load applied, it may results of forming a fracture due to overloading.

Furthermore, fouling and plugging at the pipeline will form as well. The present of moisture may also cause water hammering at the pipeline. If the natural gas use for the combustion purpose, incomplete combustion will generate if the natural gas contents of water.

2.2 EXISTANCE TECHNOLOGY: REVIEW ON THE ADSORPTION

The general term for sorption is the selective transfer to insoluble rigid particles. One or more components of gas or liquid stream are adsorbed on the surface of a solid adsorbent and separation occurs. In adsorption technology, there are two different approaches on how the adsorbate (the material that need to remove) is attached to the adsorbent (small particles in fixed that will adsorb the adsorbate); Physical adsorption and chemisorptions. Physical adsorption is the adsorption process accordingly to the van der Waals bonding. The intermolecular forces between molecules of a solid (adsorbent) and the gas (adsorbate) are greater than those between molecules (adsorbate) itself. Chemisorptions attached is based on the activated carbon where the separation occurred caused by the formation of chemical bonds between adsorbate and adsorbent.

The selection of adsorbent is depending on what type of separation takes place and mostly the criteria for adsorbent are based on:

1. High selectivity to enable sharp separations
2. High capacity to minimize the amount adsorbent needed
3. Favorable kinetic and transport properties for rapid sorption
4. Chemical and thermal stability to preserve the amount and its properties
5. Hardness and mechanical strength
6. High fouling resistance
7. Capability of being regenerated relatively low cost

Table 2.1: Commercial adsorbent for adsorption technology (Geankoplis, 1993)

Commercial adsorbents	**Descriptions**
Activated carbon	Made by thermal decomposition of wood
Silica gel	Acid treatment of sodium silicate solution
Activated alumina	Hydrated aluminium activated by heating to dry off the water
Molecular sieve zeolites	Porous crystalline aluminosilicates
Synthetic polymers or resin	Polymerizing two major types of monomers e.g Styrene and divinylbenzene

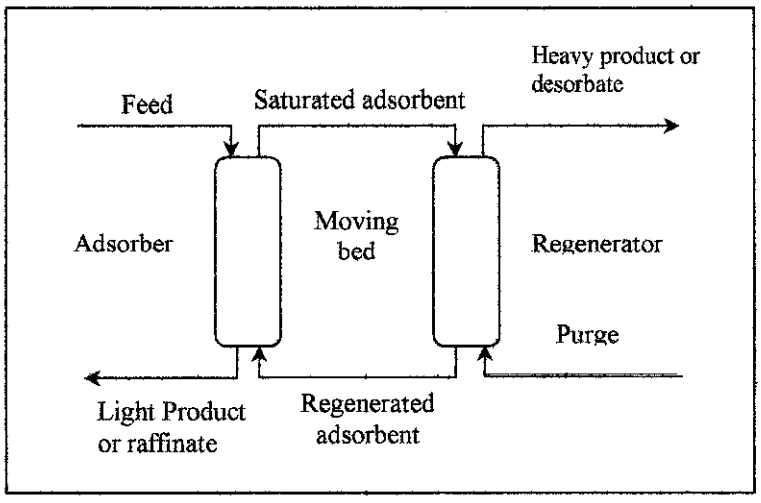


Figure 2.1: Cyclic operation with one in service and one in regeneration (Geankoplis, 1993)

2.3 PRINCIPLES AND FUNDAMENTAL OF MEMBRANE SEPARATION

The principal of a membrane process is to separate one or more constituents from two or more components system by the help of a potential driving force across a semi permeable barrier (the membrane) through which one or more of the species moves faster than another or other species.

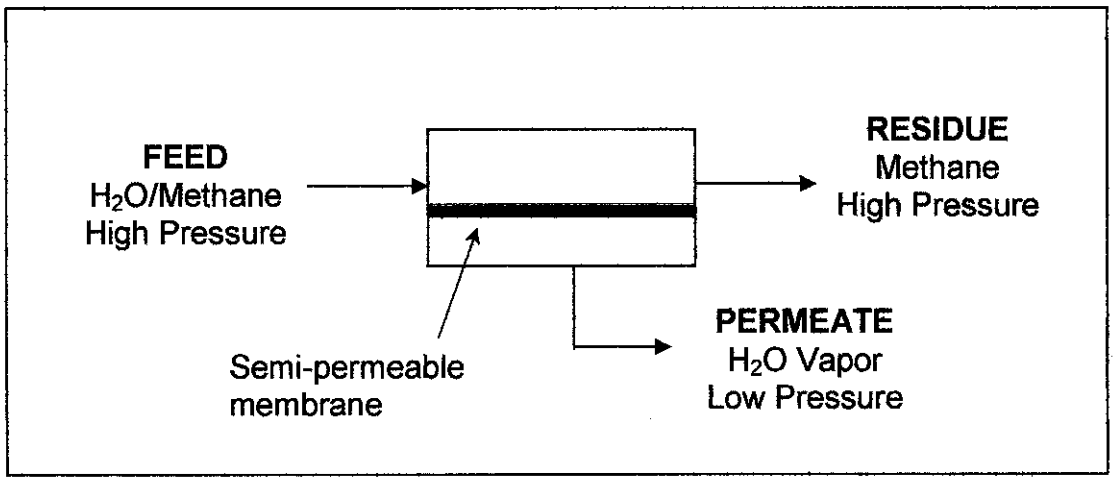


Figure 2.2: Schematic of a membrane-based separation of dehydration NG

The basic process of the membrane separation involves a feed mixture separated into a *retentate* (components that not pass through the membrane) and a *permeate* (components that passes through the membrane). Based on a single-stage membrane, separation of gas in membrane is a concentration-driven process. It is directly related to the partial pressures of the gas species and the differential pressure between the feed and the product stream.

For the natural gas dehydration, the product will be on the high pressure stream, which the residue (Noble, Stern; 1999). The feed is compressed to provide the driving force for the separation process. The membrane which acts as a semipermeable barrier, is more permeable to the water in vapor phase and thus the moisture permeate to the low pressure permeate side, due to the size of the water

molecules is smaller than methane. The remaining stream is enriched in methane and exits as the high pressure residue stream.

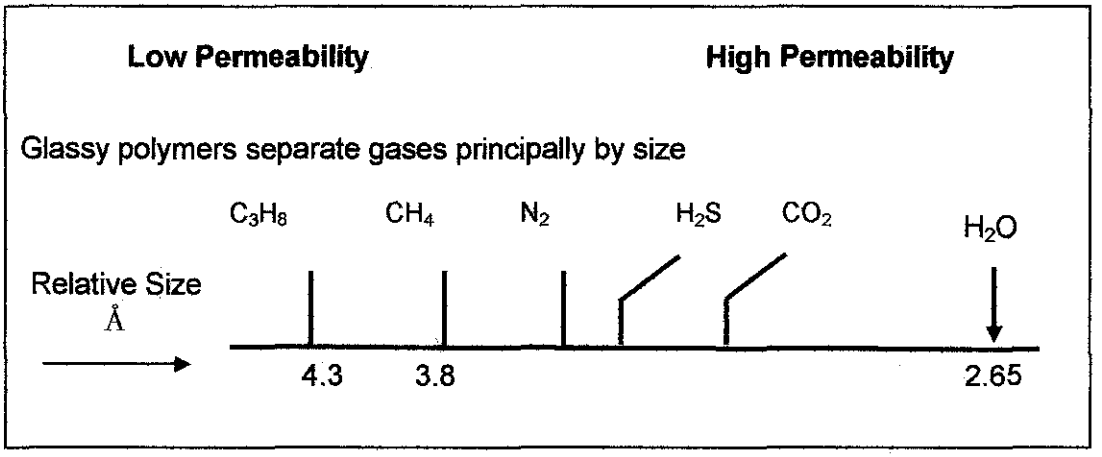


Figure 2.3: The relative size of the principle components of natural gas (Nur, 2003)

2.4 MEMBRANE SELECTION

The selection of materials for gas separation membranes requires the matching of performance characteristics of the materials available with applications (Nunes, Peinenan; 2001). Basically, there are two types of membranes on the market, which are the organic and inorganic membrane. According to the manufactures, the main advantages of inorganic membranes compared with organics membrane are; high pressure up to 10 MPa can be applied, possibilities of cleaning with steam and good back flushing possibilities to remove fouling (Noble, Stern; 1999). Thus, inorganic membrane will be the membrane selection for this case study.

The performance of membrane is determined by several affected features such as the mechanical stability, low maintenance with good space efficiency, high selectivity and high permeability. Figure 2.3 shows the principle components of natural gas with respect to the relative size. From the figure, it shows that water is small relative size; therefore it is easily separated from CH_4 using rubbery and glassy polymers.

Table 2.2: Gas membrane applications and suppliers (Noble, Stern; 1999)

Common Gas Separation	Application	Suppliers
O_2/N_2	Nitrogen generation, oxygen enrichment	Permea (Air Product), Linde (Union Carbide), A/G Technology (DOW Chemical/BOC), Asahi Glass, Osaka Gas, Oxygen Enrichment Co
H_2O/Air	Air dehumidification	Permea, Ube Industries, Perma Pure
H_2/Hydrocarbon	Refinery hydrogen recovery	Permea, Grace Membrane System (W.R.Grace)
H_2/CO	Syngas ratio adjustment	Permea, Grace Membrane System (W.R.Grace)
H_2/N_2	Ammonia purge gas	Permea, Grace Membrane System (W.R.Grace)
CO_2/Hydrocarbon	Acid gas treating, landfill gas upgrading	Grace Membrane Systems, Cynara (Dow Chemical), Separex, (Hoechst Celanese), Permea
H_2O/Hydrocarbon	Natural gas dehydration	Grace Membrane Systems, Cynara (Dow Chemical), Separex, (Hoechst Celanese), Permea
H_2S/Hydrocarbon	Sour gas treating	Grace Membrane Systems, Cynara (Dow Chemical), Separex, (Hoechst Celanese), Permea
He/Hydrocarbon	Helium separation	Grace Membrane Systems, Cynara (Dow Chemical), Separex, (Hoechst Celanese), Permea
He/N_2	Helium recovery	Grace Membrane Systems, Cynara (Dow Chemical), Separex, (Hoechst Celanese), Permea
Hydrocarbon/Air	Pollution control, hydrocarbon recovery	Membrane Technology Research, Aluminium Rheinfelden/GKSS, NKK

Table 2.2 shows some of the existence applications for the common gas separation gas with the supplier of the membrane and technology.

molecules adsorbed on the pore wall diffuse on the surface due to a concentration gradient in the adsorbed phase. Separation by condensation with liquid flow in extremely fine pores of a membrane has been shown to be quite efficient in various works for vapor mixtures of which one of the components condenses in the pores due to the capillary condensation. In this case, each pore can be blocked with the condensate to prevent the permeation of non-condensable gasses. For viscous diffusion, it describes the separation of vapor compounds of different molecular sizes through a porous membrane.

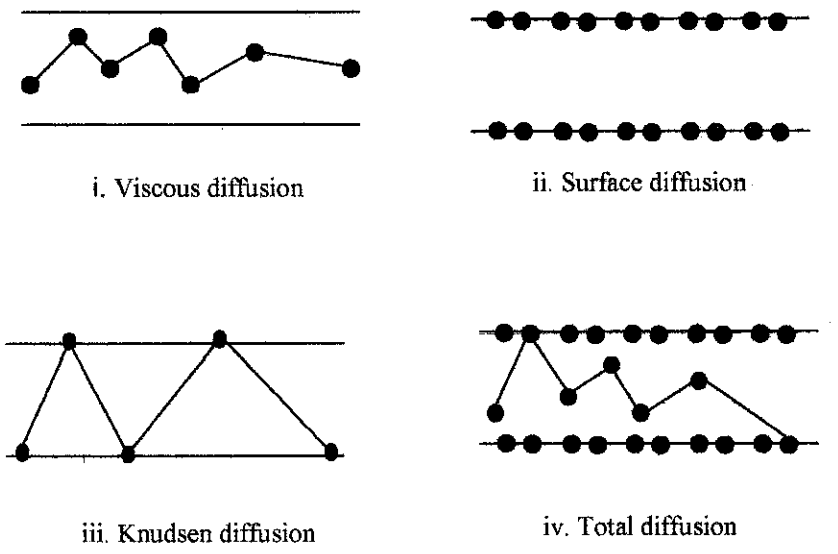


Figure 2.7: Transport mechanism: Viscous, Surface, Knudsen and Total Diffusion (Roslee, 2001)

where $\overline{P}$ is the average pressure and μ is the viscosity of the species gas i. The partial pressure of the 'faster' gas should be higher than downstream partial pressure.

Surface diffusion is the other mechanism that takes into account for the gas separation. Theoretically, it can occur in small pore diameter membrane. The smaller the pore size, the surface adsorption become more noticeable and particularly if the gas is condensable. The surface diffusivity can be expressed from the correlation,

$$D_s = 1.6x10^{-2} \exp\left[0.45\frac{(-\Delta H_{ads})}{mRT}\right] \tag{2.4}$$

where m = 2 for conducting adsorbents and m = 1 for insulating adsorbents, ΔH_{ads} is the specific enthalpy difference of adsorption of a species at T and P. The modified equation obtained for that will have the pore size relationship is:

$$D_s = 1.6x10^{-2} \exp\left[0.45\frac{(-\Delta H_{ads})}{mRT}\right]\frac{t_m}{r_p} \tag{2.5}$$

where $\frac{t_m}{r_p}$ is a dimensionless equation which is already estimated and obtained a value of 0.0001 (Zurainun, 2003).

The bulk diffusivity correlations can be refers as,

$$D_B = \frac{1x10^{-7} T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}}{P\left(\upsilon_A{}^{1/3}+\upsilon_B{}^{1/3}\right)^2} \tag{2.6}$$

where D_B = Bulk diffusion for species gas i and v is the volume diffusion of atom and structure which can be obtained from the Perry's Chemical Handbook.

The final relations to predict the diffusivity of a binary gas pair A and B molecules which was obtained by correlating many recent data and uses atomic values (refer to Table A3 in Appendices) is as equation,

$$D_{AB} = \frac{1.00x10^{-7}T1^{.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}}{P\left[(\Sigma v_A)^{1.3}+(v_B)^{1/3}\right]^2} \qquad (2.7)$$

where D_{AB} is refer as bulk diffusivity, Σv_A and Σv_B are sum of structural volume increment.

2.8 GAS PERMEABILITY

The permeability of the gas through membrane is very difficult to obtain an accurate value. The mathematical equations for the individual permeability is related as below,

$$P_v = P_i D_v \qquad (2.8)$$

where P_V = Viscous Permeability for species gas i, P_i = Permeability for species gas i, D_V = Viscous diffusion for species of gas i

$$P_K = P_i D_g \tag{2.9}$$

where P_K = Knudsen Permeability for species gas i, P_i = Permeability for species gas i, D_g = Gas diffusion

$$\mathrm{P_S} = \mathrm{P_i} \frac{1}{\varepsilon} D_S \rho_M f \tag{2.10}$$

where Ps = Surface Permeability for species gas i, ρ_M = Membrane density, f = Equilibrium loading factor.

$$P_i = \frac{\varepsilon}{zRT\tau} \tag{2.11}$$

where P_i = Permeability factor for species gas i, ε = Porosity of membrane, z = Compressibility factor and τ = Tortuosity

The derivation of the permeability for the combination of Knudsen, diffusion and viscosity mechanism can be expressed as

$$P_i = \frac{\varepsilon}{z\tau RT}\left\{\frac{\mathrm{Pr}_p^{\,2}}{8\mu} + \left(\frac{1}{1/D_i + 1/D_k}\right) + \frac{1}{\varepsilon}\left(D_s \rho_m f\right)\right\} \tag{2.12}$$

which P_i has the unit $[mol.s^{-1}][m][m^{-2}][kg^{-1}.m.s]$ and f is the equilibrium loading factor $(m^3.kg^{-1})$.

2.9 PROCESS DESIGN

The process design of the membrane system involves the determination of the system size and configuration necessary to meet the project scope and specifications. Process control of gas separation units typically involved around four membrane operating parameters; temperature, pressure, flowrate and membrane area (Nunes, Peineman 2001). For this project, the author investigate the permeability effect with respect to the temperature, pressure, pore size and feed concentration.

2.9.1 Effect of the Temperature and Pressure

Based on the analysis done by Roslee (2001), the permeability of the gas will be more effective as the temperature is increased. Somehow, the analysis which was done by Cho et al.,(1995) found that the permeability is poorer as the temperature is increase which used Υ-Al_2CO_3 type of membrane. But then all the effect of the permeability was obvious when the ratio of the pressure is at low value. All membrane modules have upper limits of operating temperature. The permeability, P_A can be related using the equation above with absolute temperature, T;

$$P_A = K_A \exp\left(\frac{-E_A}{RT}\right) \tag{2.13}$$

where K_A and E_A are the empirical correlation coefficient determined from the laboratory or data from the field.

Pressure is another operating factor that will contribute to the changed of the permeability of the gas species. A higher feed pressure increases the permeation of the gas through the membrane, and so the requires stage cut can be achieved with less membrane areas.

$$\frac{y_p}{1-y_p} = \frac{\alpha^*\left[x_o - \left(\frac{p_l}{p_h}\right)y_p\right]}{(1-x_o) - \left(\frac{p_l}{p_h}\right)(1-y_p)} \tag{2.16}$$

where p_h is the total pressure in the high pressure side; p_l is the total pressure in the low pressure permeate side; x_o is the mole fraction at the reject side; y_p is the mole fraction at the permeate side; x_f is the mole fraction at the feed side; α^* for the ideal separation factor. This equations relates y_p, the permeate composition, to x_o, the reject composition and the ideal separation factor α^*. The separation factor is defined as

$$\alpha^* = \frac{P'_A}{P'_B} \tag{2.17}$$

where P'_A and P'_B are the permeability for species A and B respectively. From the overall balance below

$$q_f x_f = q_o x_o + q_p y_p \tag{2.18}$$

by dividing q_f and solving it will obtain the correlations as below;

$$x_o = \frac{x_f - \theta y_p}{(1-\theta)} \tag{2.19}$$

CHAPTER 3

METHODOLOGY

3.1 PROCEDURE IDENTIFICATION

The main objective of this project is to model a simulation of the dehydration of natural gas through membrane by analyzing the permeability with respect to the pressure, temperature, pore size and as well as the feed concentration. All the data gathered from the thesis, journal, and reference book is highlighted and analyzed to use for the modeling purposes. The study of the correlations is very important to obtain an exact equation for the dehydration of natural gas. Then, the equations are analyzed and finalized to produce the graph. The equation that used for modeling had to ensure the units involve are constant through the entire step and similar with other terms used. If the graph far away from the expectation with the theory, the equation had to be analyzed again until the exact trend is obtained.

Based on the mathematical equation as mentioned before, the modeling was done using MathCAD and come out with the related graph to be interpreted. The properties of the water and methane need to identify and determine first before model any mathematical equation as this properties is the input to the simulation.

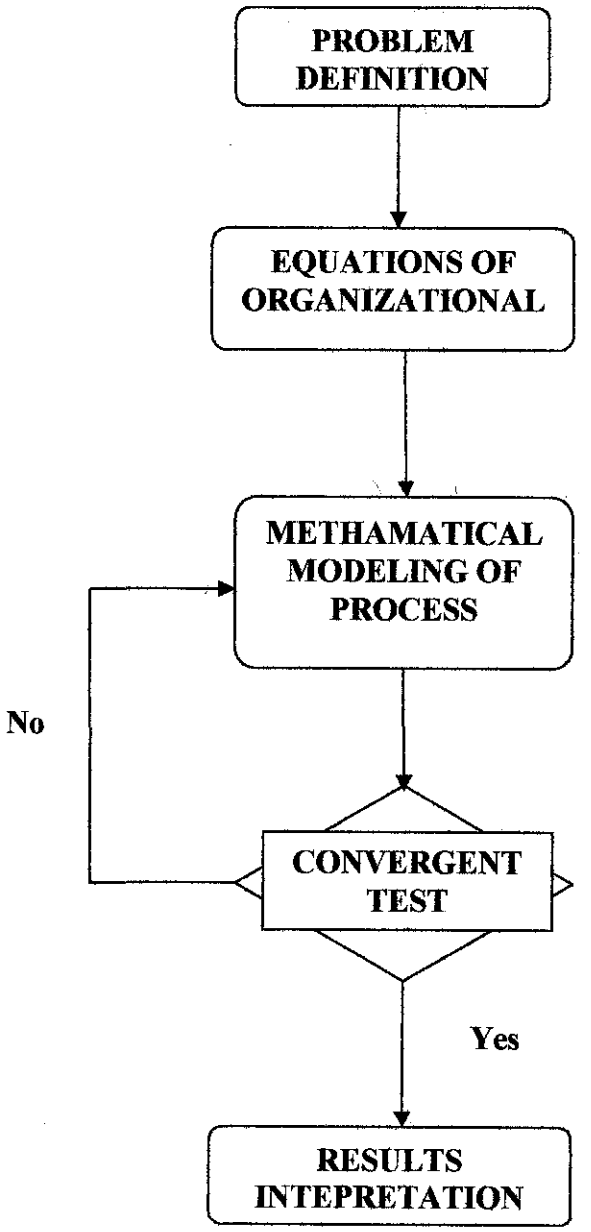


Figure 3.1: Methodology of project work

3.1.1 Problem Definition

When the problem associated has been defined and analyzed the student has to understand the basic concept of the project. The basic understanding of the project title and the background of the study is the most important. After then, the scope will be narrow to the specified objectives.

3.1.2 Equations of Organizational

From the literature review, journals and other materials that gathered through research, all the equations and correlations are analyzed and study before proceeding to the modeling. Mathematical model from equations (2.1) to (2.19) are used to determine the permeability with respect to temperature, pressure, pore size and feed concentration, and selectivity with respect to the pressure, temperature and feed concentration.

3.1.3 Mathematical Model of Process

The most related mathematical equation is finalized and used. Recheck and ensure that all the graphs and results is in the expected range, and if the results obviously show the different patter, re do the modeling process until the results is obtained.

3.1.4 Convergent Test - Graphs

From the modeling, results come out in the graph pattern rather than table to clearly see the results. The graphs of permeability and selectivity analysis are both plotted:

1. Permeability versus pore size (Figure 4.1, 4.2, 4.7) with other parameters constant [T=350K, P=60 bar, pore size=0.2 – 2nm, ξ=0.272, τ=0.3676].
2. Permeability versus pressure (Figure 4.3, 4.4 and 4.9) with other parameters constant [T=350K, P=30-75 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676].
3. Permeability versus temperature (Figure 4.5, 4.6, 4.10) with other parameters constant [T=350 – 550 K, P=60 bar, pore size=0.2 – 2nm, ξ=0.272, τ=0.3676].
4. Permeability versus moisture contents (Figure 4.8) with other parameters constant [T=350 K, P=60 bar, pore size =0.4 nm, ξ=0.272, τ=0.3676].
5. Selectivity versus pressure with different pore size (Figure 4.11) with other parameters constant [T=350 K, Pressure = 30 – 75 bar, pore size=0.4 and 10 nm, ξ=0.272, τ=0.3676, θ=0.02, y_p=0.25].
6. Selectivity versus temperature (Figure 4.12) with other parameters constant [T=350 550 K, Pressure = 60 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676, θ=0.02, y_p=0.25, x_F=0.9 and 0.94].

3.1.5 Results Interpretations

From the graph obtained, analyze and interpret the results.

Table 3.1: Properties of methane and water (Perry's Handbook)

	MW (kg/kg-mol)	**T_c (K)**	**P_c(bar)**	Σv_A	**Molecular Size (Å)**
CH_4	16.043	190.6	46	24.42	3.8
H_2O	18	647.3	220.9	9.44	2.65

The critical temperature and pressure (T_c and P_c) are used to obtain the compressibility factor in order to determine the permeability of the gas separation. The heat vaporization of the water is determine from the reference book (Felder,

Rousseau, 2000), which gives the value 46056 J/mol. The physical properties of membrane are specified based on the market's specification.

Table 3.2: Properties of PEBAX membrane (Nur, 2003)

	Thickness, tm	**Tortuosity, τ**	**Porosity, ξ**	**Pore size, nm**
PEBAX	6 nm	3.676	0.272	0.4

Simplification of the results had been listed in part 3.1.4. For the case of varying the size of the pore, the size range between 0.2 to 2 nm is investigated. The graph was interpreted and discuss on Chapter 4. The change in pore size will affect the viscous and Knudsen diffusivity and permeability as both mechanisms is change with respect to the change in pore size.

For varying in pressure, the range pressure between 30 to 75 bar is investigated. The viscous diffusion will varies with the change of pressure as the pressure will affect the viscous mechanism to the permeability.

The temperature varies from 350 to 750 K. The three mechanisms are change due to the changes of the temperature as all the mechanism is closely related to the change in temperature.

Table 3.3: The range of the parameters that had been studied

Parameters	**Range**
Pore size	0.2 – 2.0 nm
Temperature	350 – 550 K
Pressure	30 – 75 bar
Moisture Content	1 – 5 %

3.2 TOOL

The modeling is the experimental process based on the mathematical equation proven using MathCAD software. The MathCAD allows individual engineers to calculate, graph, and communicate technical ideas through visual format. Figure 3.2 below is the example of the algorithm permeability of water

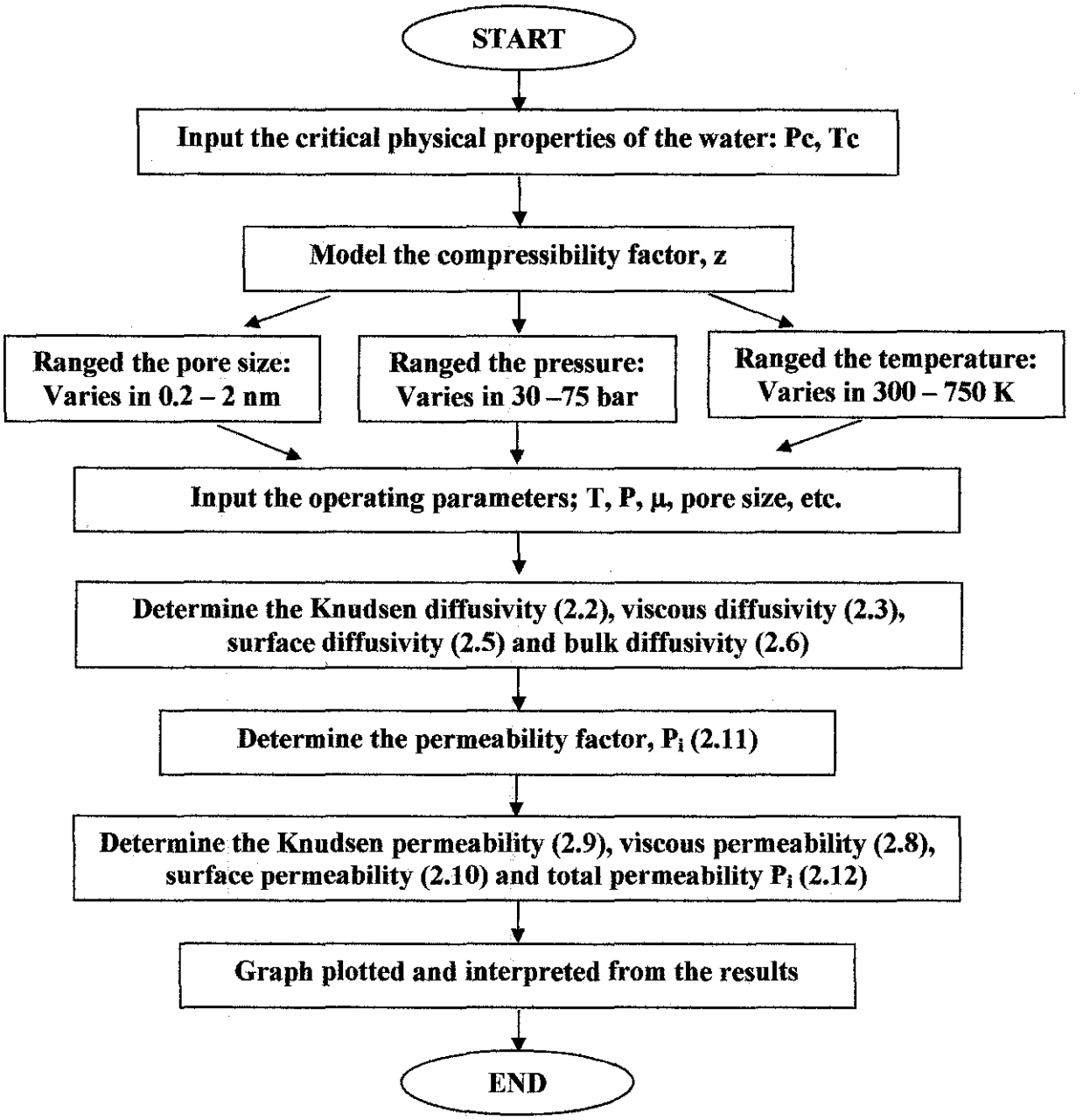


Figure 3.2: Example of the input to the MathCAD

CHAPTER 4

RESULTS AND DISCUSSION

This section is the final results after running the modeling of the process until the expected graph was observed to have. The analysis involved the parameters such as temperature, pressure, pore size, feed concentration etc.

4.1 PERMEABILITY OF PURE GAS VARIES IN PORE SIZE

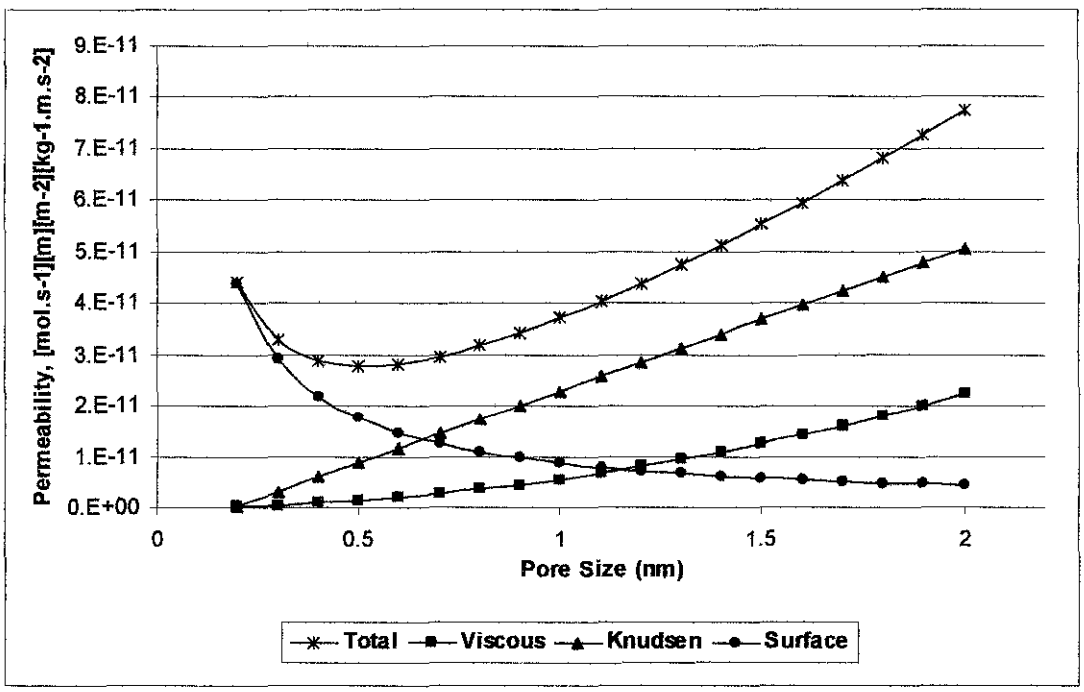


Figure 4.1: Permeability of pure moisture versus pore size

[T=350K, P=60 bar, pore size =0.2 – 2nm, ξ=0.272, τ=0.3676]

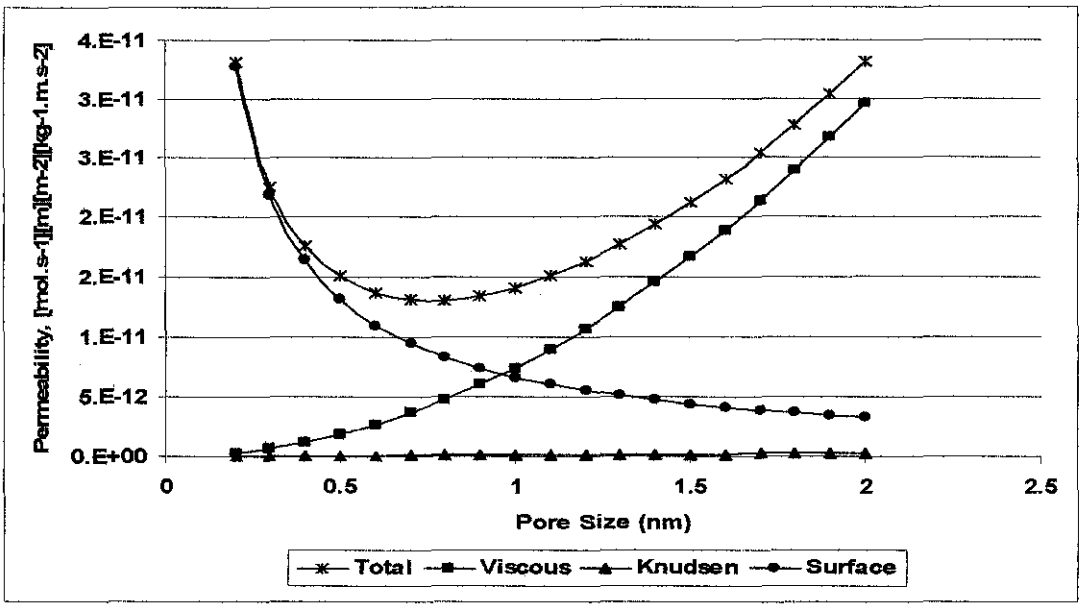


Figure 4.2: Permeability of pure methane versus pore size
[T=350K, P=60 bar, pore size =0.2 – 2nm, ξ=0.272, τ=0.3676]

Figures 4.1 and 4.2 show the trend of permeability of pure moisture and methane against the pore size ranging from 0.2 to 2 nm with constant other parameters. Both graphs show the permeability due to total and individual mechanisms of diffusion, which are Knudsen diffusion, viscous diffusion and surface diffusion.

Generally, as the size of the pore increases, the total permeability (*) increases started from 0.8 nm onwards for pure methane and 0.6 nm onwards for pure moisture. The increasing of the pore size means the pore is larger and more gas species would diffuse into the larger pore size. This allowed the diffusion rate of the gas species increases and directly increases the permeability. For the pore size ranging below 0.8 nm (for pure methane) and below 0.6 nm (for pure moisture), the permeability drop gradually as the pore size increase. This condition occurred due to the individual mechanism of the diffusion behavior that particularly gives affect to the total permeability.

According to both graphs, surface permeability decreases as the size of the pore increases. It is predominantly at pore size ranged in between 0.2 to 0.6 nm (for pure moisture) and 0.8 nm (for pure methane) which totally gives the effect to the total permeability to drop as the pore size increase. This happen because the smaller the pore size of the membrane, the wall between the pore becomes nearer to each other. For the small size of pore (basically ranged at the predominant), the water molecules experience a strong interaction with the wall and surface of the pore. As the walls come even closer to each other, the minimum potential is raised due to overlap of the repulsive part of the energy until the pore becomes impermeability (Noble, Stern; 1999).Thus, it allows for the gas species to predominantly diffuse due to the surface mechanism. If the walls are far apart, minimum potential occur due to attractive forces of the molecule-wall interaction.

The Knudsen diffusion behaves differently between the pure moisture and methane. As the pore size increases, the permeability for pure moisture is nearly increased linearly. However, the permeability for the pure methane can be neglected and could be concluded that the permeability is independently with the increasing pore size. The moisture molecules experience more collision with increasing pore size due to smaller size of the moisture molecules compared to methane molecules. Thus, the mean free path (λ) increased, results for the λ, to have a larger path than average pore dimension. So that allows the pure water experience the Knudsen diffusion while pure methane independently to the Knudsen diffusion.

The derivation of the viscous diffusivity (equation 2.3) shows that it is inversely related to the viscosity of the gas species and proportionally related to the size of the pore. Thus, the larger the size of the pore, the diffusivity is increased and directly increased the viscous permeability (equation 2.8). From the both graphs, it is obviously show the increased in pore size, the viscous permeability is gradually increased.

4.2 PERMEABILITY OF PURE GAS VARIES IN PRESSURE

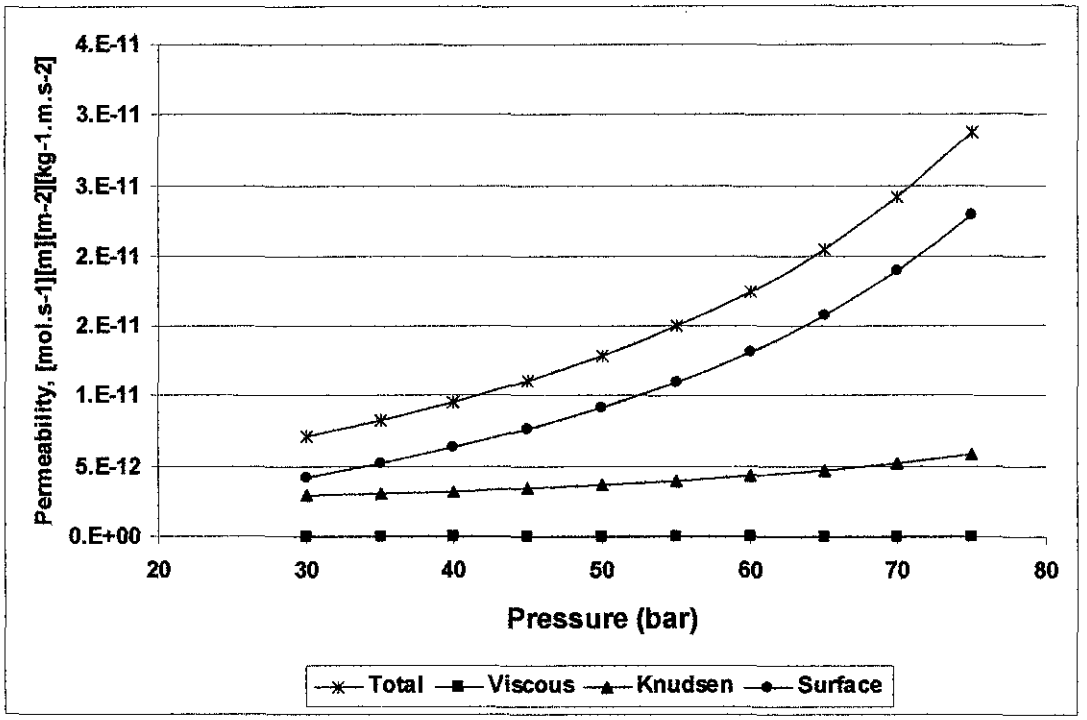


Figure 4.3: Permeability of pure moisture versus pressure

[T=350K, P=30-75 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676]

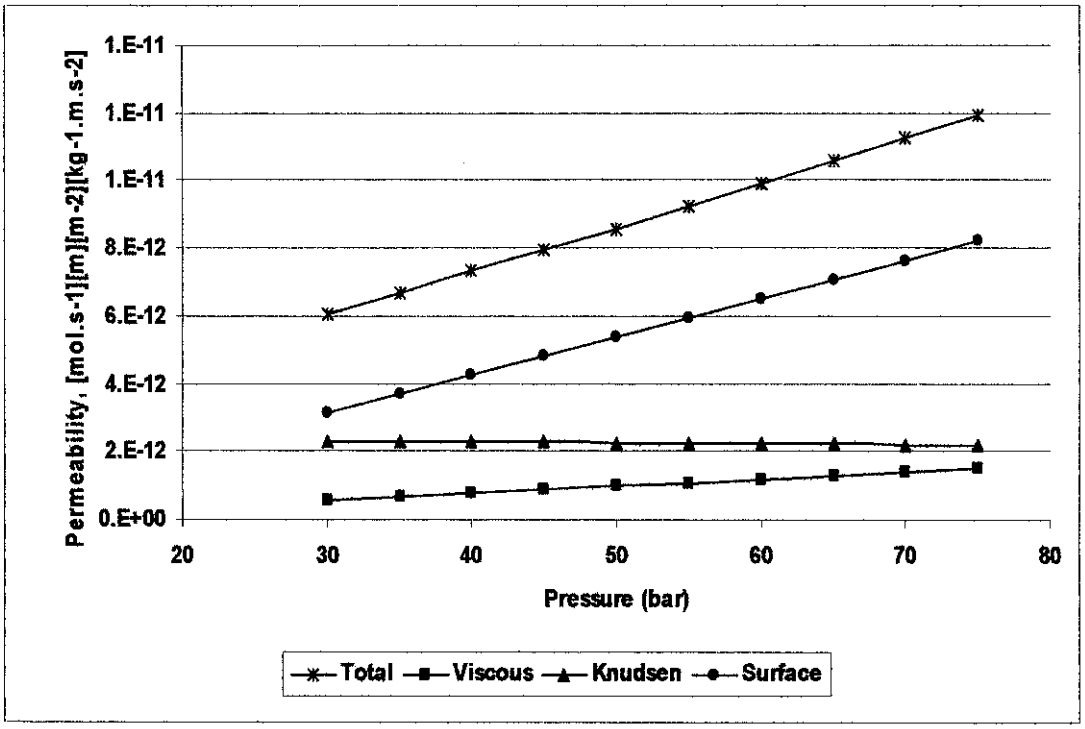


Figure 4.4: Permeability of pure methane versus pressure
[T=350K, P=30-75 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676]

Figures 4.3 and 4.4 show the trend of permeability of pure moisture and methane against the pressure ranging from 30 to 75 bar with constant other parameters. Both graphs show the permeability due to total and individual mechanisms of diffusion, which are Knudsen diffusion, viscous diffusion and surface diffusion.

Generally, as the pressure increased, the total permeability (*) is increased as well. From the Figure 4.3, it is clearly observed that the higher the pressure, the greater/steeper the slope of total permeability. It shows that the permeability of the moisture is sensitive to the increment of the pressure. However, the total permeability (*) for methane is almost linearly related to the increasing in pressure. The relationship of the pressure and permeability is best described by the individual mechanism diffusivity that is directly affected the total permeability.

Based on both graphs, as the pressure is increased, the surface permeability for both becoming more important due to the small pore size of membrane used, which is 4nm. When pressure increases, the concentration of the gas molecules per surface area of the membrane is increased. Thus, the interaction of the molecules with the surface of the membrane will increase and result for the permeability of the surface mechanism became predominant.

The affect of the viscous permeability is observed only for the pure methane while it is independently related to the permeability of pure moisture. From figure 4.4, as the pressure increases, the permeability is linearly increased. The viscous permeability has very close relationship with the viscosity of the gas species and the compressibility factor. The pressure increase will result to the increasing viscosity (μ) and decreasing compressibility factor (z). Thus, the viscous permeability will slightly increase.

For Knudsen permeability of the water molecules, it affect reversely if compare to the methane molecules. As the pressure increases, for the pure water, the Knudsen permeability increases slowly while for the pure methane, it decreases very slowly.

4.3 PERMEABILITY OF PURE GAS VARIES IN TEMPERATURE

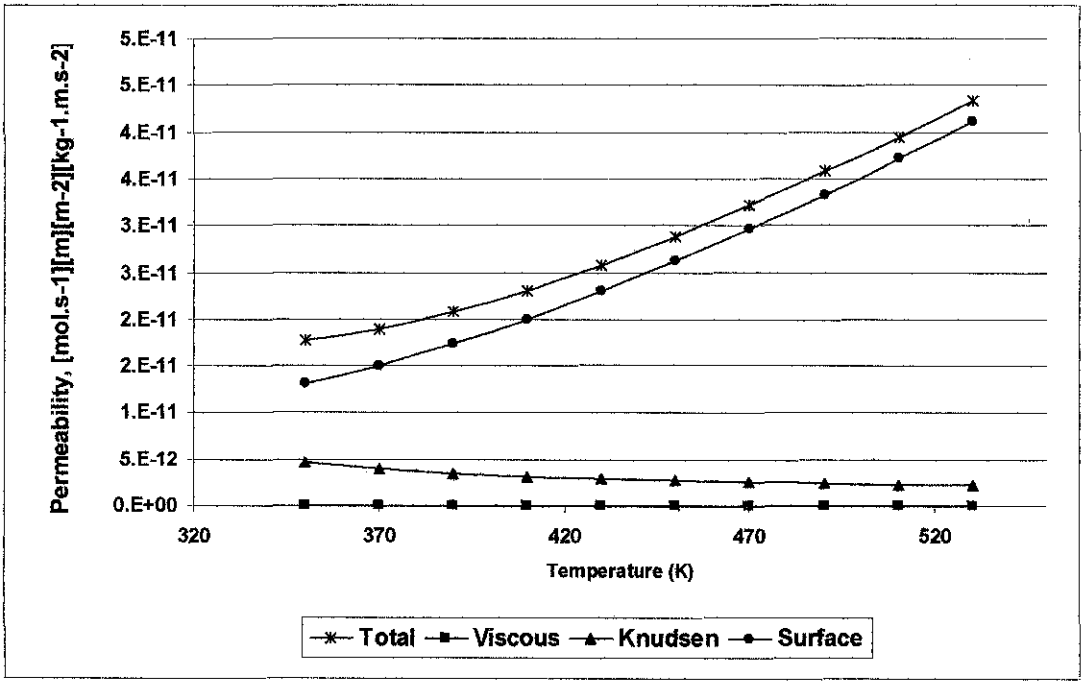


Figure 4.5: Permeability of pure moisture versus temperature

[T=350 – 550 K, P=60 bar, pore size=0.2 – 2nm, ξ=0.272, τ=0.3676]

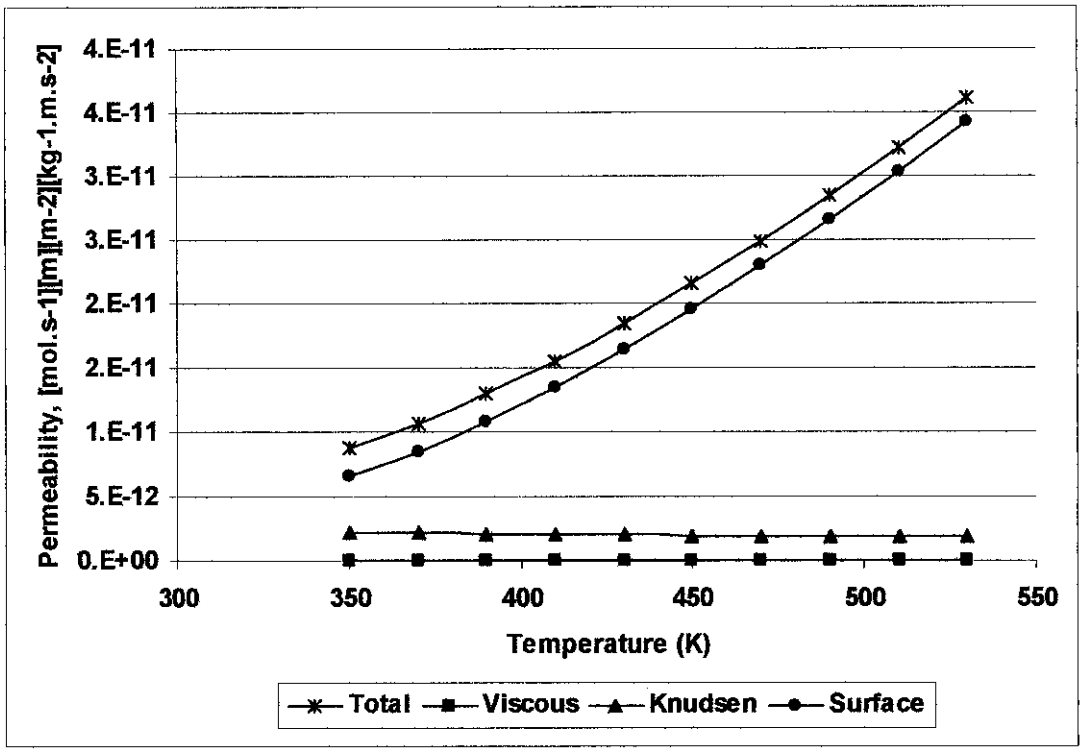


Figure 4.6: Permeability of pure methane versus temperature
[T=350 – 550 K, P=60 bar, pore size=0.2 – 2nm, ξ=0.272, τ=0.3676]

Figures 4.5 and 4.6 show the trend of permeability of pure moisture and methane against the temperature ranging from 30 to 75 bar with constant other parameters. Both graphs show the permeability due to total and individual mechanisms of diffusion, which are Knudsen diffusion, viscous diffusion and surface diffusion.

Generally, as the temperature increased, the total permeability (*) is increased as well. From the Figure 4.6, it is clearly observed that the higher the temperature, the greater/steeper the slope of total permeability. It shows that the permeability of the moisture is sensitive to the increment of the pressure. However, the total permeability (*) for moisture is almost linearly related to the increasing in temperature. The relationship of the temperature and permeability is best described by the individual mechanism diffusivity that is directly affected the total permeability.

For both graphs, the most bottom curve that nearly lies to the x-axis is the permeability of the viscous mechanism and the increasing of temperature gives no effect to the viscous permeability. The effect of the viscous is less important due to the small pore size is applied for this modeling.

From both graphs, the surface permeability is increased with the highest rate compared to the other two mechanisms. This directly shows that the surface permeability is the predominant mechanism takes place as the temperature is increased. Theoretically, the surface mechanism is applicable when the mean free path, λ, is less than the pore size. However, as small pore size, 4nm is used, the mean free path is more than the pore size in which causes a lesser collision between the gas molecules with another molecules rather than collision with the membrane.

While the Knudsen permeability is decreased with increasing temperature for both graphs. The shorter mean free path (λ) of the molecules which cause by the increasing pressure, will result to the lesser collisions with the pore walls than with each other. This explains why the Knudsen permeability is decreased with the increasing temperature. According to Noble, separation by Knudsen diffusion has some limitations because only lighter component (e.g H_2) can be preferentially removed. Thus, this mechanism has a small contribution to the diffusion of the water vapor molecules into the membrane.

4.4 PERMEABILITY OF GAS MIXTURE VARIES IN PORE SIZE

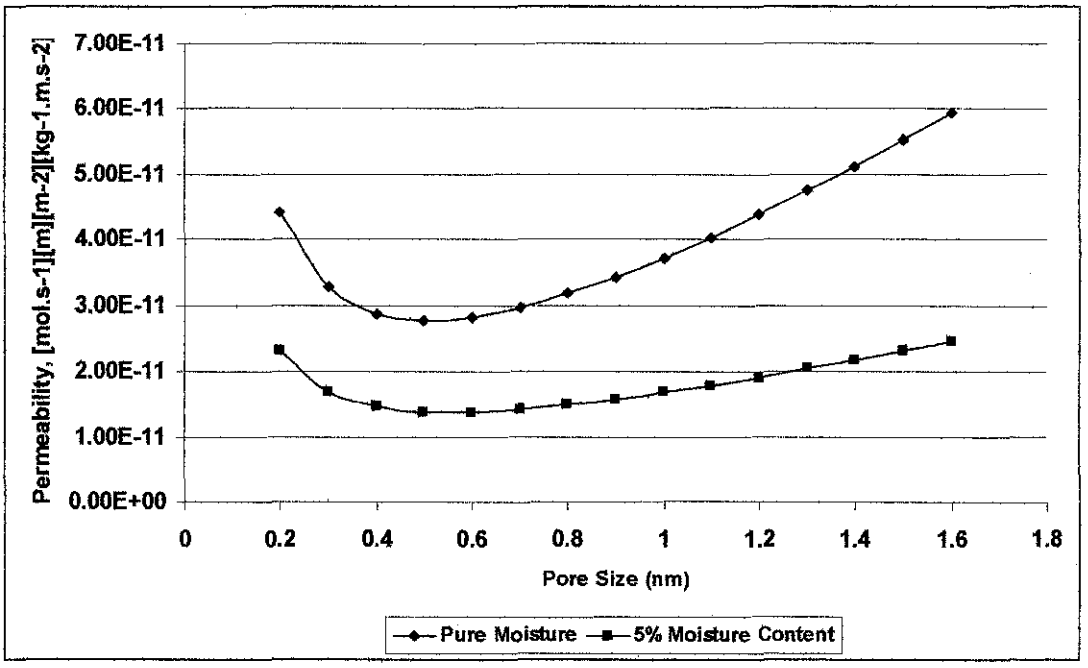


Figure 4.7: Comparison between the pure moisture and 5-95% mixture varies in pore size [T=350K, P=60 bar, pore size=0.2 – 1.6nm, ξ=0.272, τ=0.3676]

Figure 4.7 shows the permeability of pure moisture and mixture of 5% moisture content and 95% methane against the pore size which varies from 0.2 to 1.6nm while constant other parameters. The comparison was only analyzed between the pure moisture and gas mixture as the permeability of pure methane is much higher which is to the power of -11 and it is difficult to plot in the same graph to see the different. The trend of both curves is similar to each other. It is shows that even though the small amount of concentration contains in the methane, the permeability is increased but for only small increment. As the pore size increased, the mixture curve give almost similar values and behaves approaches the water properties. Based on this graph, it is clearly shows that the total permeability is only best suited when the pore size is higher than 0.6nm as from that point towards; the permeability will increase as the pore size increases. The reason is due to the individual transport mechanism which is already discussed in part (4.1).

4.5 PERMEABILITY OF GAS MIXTURE VARIES IN MOISTURE CONTENTS

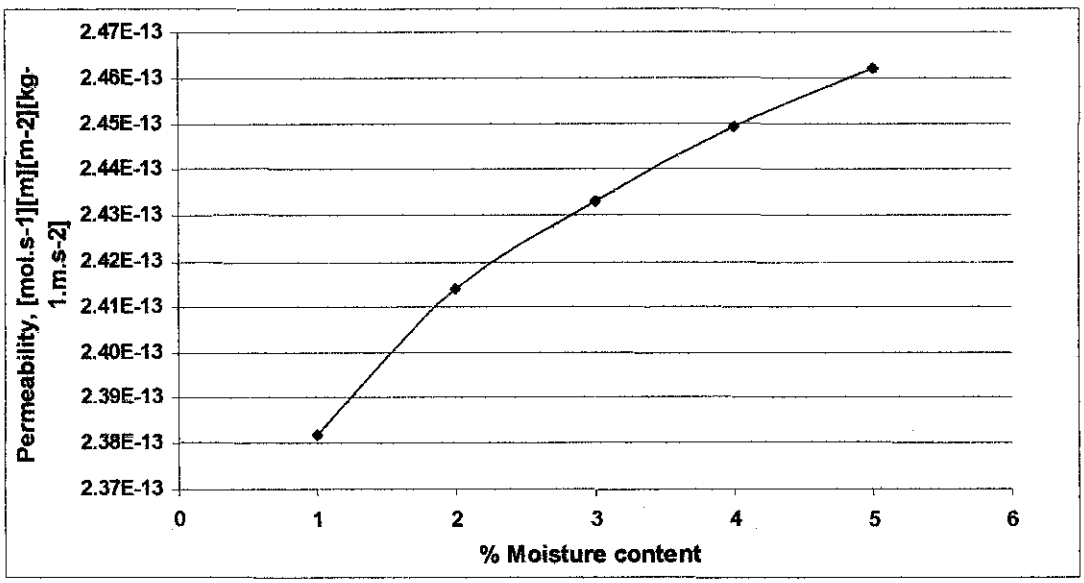


Figure 4.8: The permeability of the mixture when varying the moisture contents from 1% to 5% [T=350 K, P=60 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676]

Figure 4.8 shows the total permeability of the mixture when varying the moisture ranging from 1 to 5% with constant other parameters. Based on the result obtained, the increasing of the moisture content increases gradually the total permeability. The reason is related to the individual transport mechanism which is considered in the study.

Generally, when the moisture content increased, the amount of water per volume of the mixture is increased (greater amount of moisture molecules) and more diffusion takes places (as moisture diffuse at faster rate compared to methane) which directly increase the permeability. The higher the water contains, the viscous effect does not give a big effect to the total permeability and for both Knudsen and surface permeability increases.

4.6 PERMEABILITY OF GAS MIXTURE VARIES IN PRESSURE

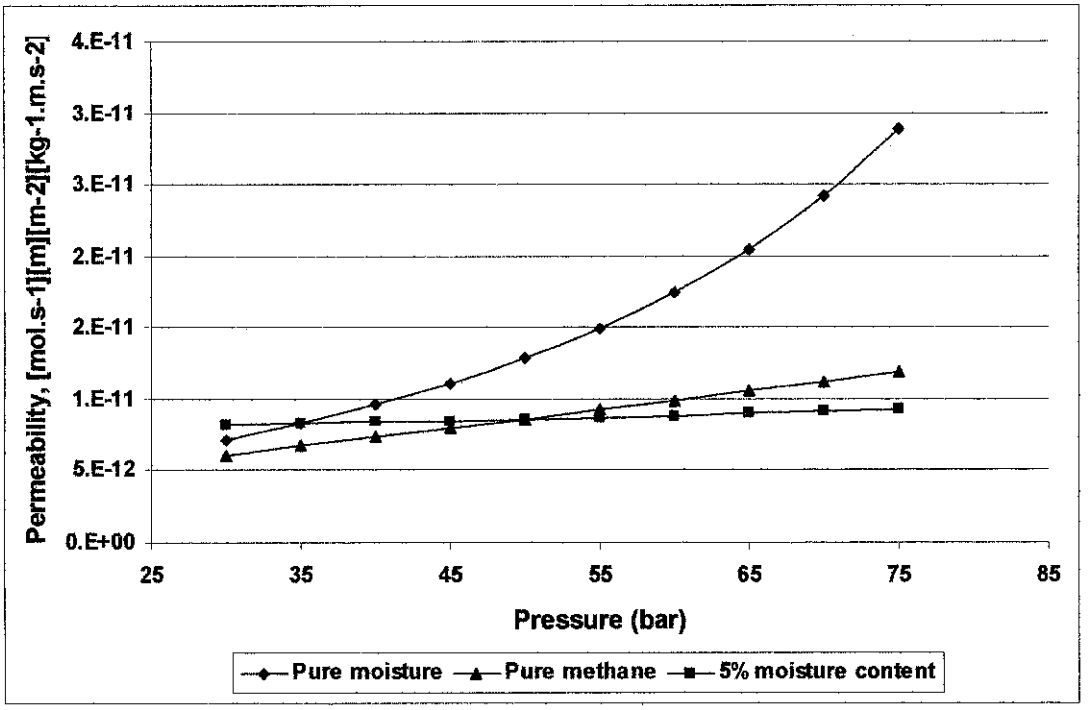


Figure 4.9: Comparison between the pure gas and the gas mixture varying in pressure [T=350K, P=30-75 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676].

Figure 4.9 shows the comparison between the permeability of pure water, pure methane and the mixture of 5%-95% (5% moisture content). Based on the graph, the pure moisture is the highest permeability, and increases significantly as the pressure increases compared with other two. This happen because the diffusion rate of the water molecules moves faster than the molecules of the methane. As the mixture increases the water contents, the permeability is observed to increases. When the pressure increases, the water molecules move faster than the methane and it is able to permeate through the membrane compares to the methane.

4.7 PERMEABILITY OF GAS MIXTURE VARIES IN TEMPERATURE

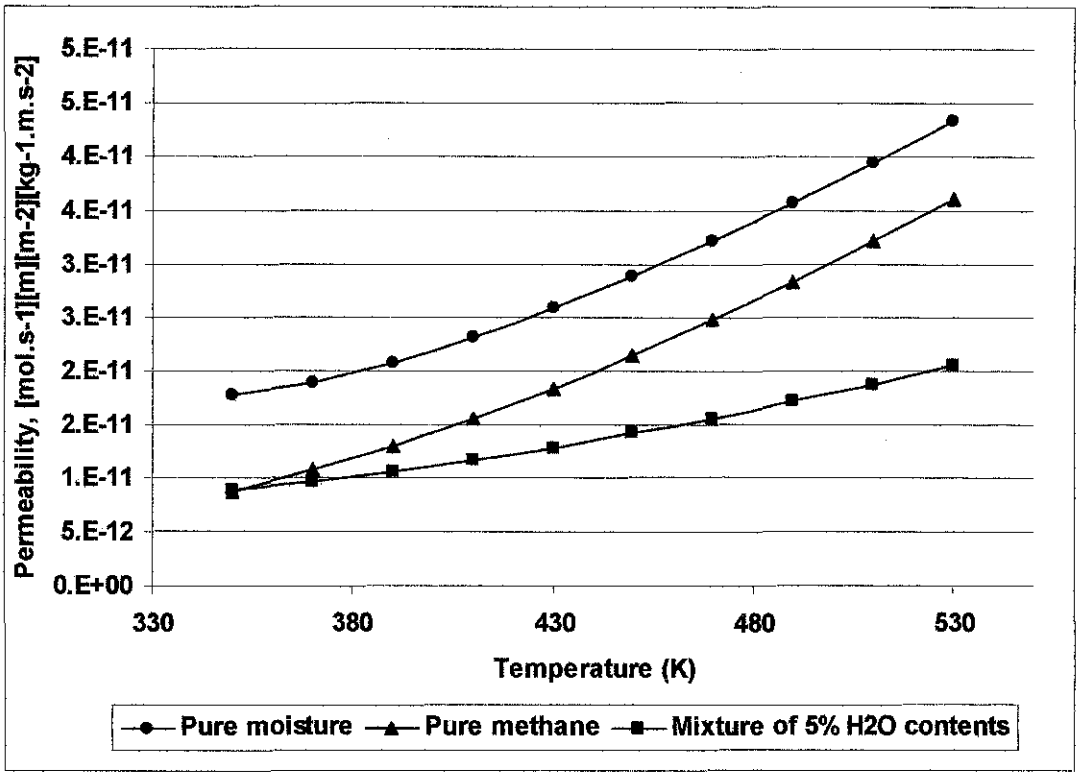


Figure 4.10: Comparison between the pure gas and the gas mixture varying in temperature [T=350 – 530 K, P=60 bar, pore size=0.4 nm, ξ=0.272, τ=0.3676]

Figure 4.10 shows the permeability of the pure gas and the mixture of 5%-95% with respect to the temperature ranging from 350 to 530 K. Based on the graph above, as the temperature increases, the pure gas permeates higher than the mixture. This happen because the increasing temperature results to more rate of collision occur as the molecules gain higher kinetic energy to move randomly. As the water molecules is bigger than the methane molecules, more void space will allow the water molecules to collide more frequently than the molecules of the methane. Thus, the pure water will result to a higher permeability compared with other two. For the mixture of water and methane, the permeability is poorer than the pure gas as the temperature increases.

4.8 SELECTIVITY OF THE MOISTURE AND METHANE VARIES IN PRESSURE WITH DIFFERENT SIZE OF PORE

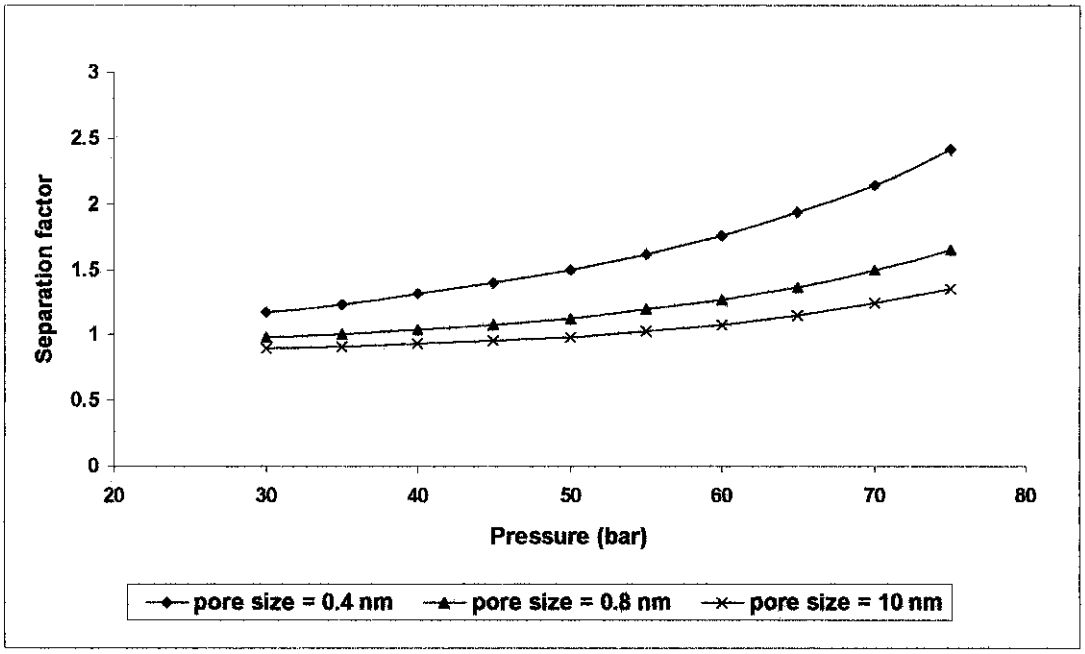


Figure 4.11: Selectivity of the water and methane through the membrane when varying in pressure at different pore size [T=350 K, Pressure = 30 – 75 bar, rp=0.4 and 10 nm, ξ=0.272, τ=0.3676, θ=0.02, y_p=0.25]

Figure 4.11 shows the selectivity which defined as separation factor with respect to the changed in pressure from 30 to 75 bar at pore size equal to 0.4, 0.8 and 10 nm. Based on the graph, the selectivity is the best at the high pressure with lower pore size. As the pressure increases, there will be a higher driving force exerted to the membrane. Thus, the selectivity is increased as it will enhance the separation between water and the methane. When the pore size increases, there is a large drop in the surface permeability although the Knudsen and viscous permeability is increased at higher pore size. The larger the pore size, the diffusion will occur more and increases the separation factor.

4.9 SELECTIVITY OF THE MOISTURE AND METHANE VARIES IN TEMPERATURE

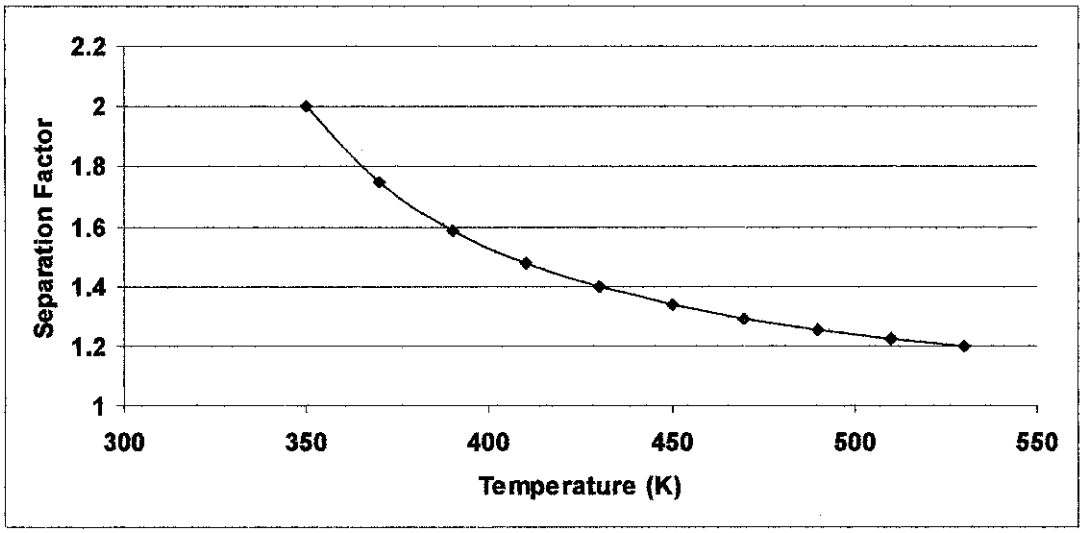


Figure 4.12: Selectivity of the water and methane through the membrane when varying in temperature at different pore size [T=350-530 K, Pressure = 60 bar, pore size=0.4, ξ=0.272, τ=0.3676, θ=0.02, y_p=0.25]

Figure 4.12 shows the permeability of the separation factor versus temperature with different size of the pore. Increasing the temperature at the small pore size give no to much different compared to the separation factor. According to the graphs, the deviation value of the separation factor for different size used gives almost the same values.

CHAPTER 5

CONCLUSION

The simulation model for predicting performance of membrane for the dehydration of natural gas using inorganic membrane separation is developed using MathCAD software. The simulation model has been carried out to study the parameters such as temperature, pressure and pore size of the pure H_20.

The permeability is based on the transport mechanisms which are surface, Knudsen and viscous permeability. For different properties of different gas species, the mechanisms behave in different pattern with respect to the pressure, temperature and the size of the pore.

Generally, based on this study, it could be concluded that the trend of permeability with parameters are as follow:

a) As the pores size, pressure and temperature are increased, total permeability for the pure gas (methane and moisture) is increased.

b) As the pores size, pressure, temperature and moisture content are increased, total permeability for the mixture (methane and moisture) is increased

c) The total permeability is observed to strongly depend on the transport mechanism which for this study, three mechanism are take into account;

Knudsen, viscous and surface diffusivity. Chapter 4 discussed in details the behavior of those transport mechanisms.

d) The increasing in pressure and pore size gives the result of gradually increasing the separation factor (selectivity) and enhance the separation of the moisture from methane.

e) The separation factor is drop when the temperature is increased.

The results obtained are satisfied and fulfilled all the objectives of this study. Throughout the study, it could be concluded that the permeability is most favorable at higher pore size, temperature, pressure and moisture contents. The separation of moisture from the methane is most enhanced at the higher pressure and pore size but at lower temperature. By using the selected membrane with pores size equals to 0.4 nm, ξ=0.272 and τ=0.3676, the separation is proved to occur through the mathematical modeling using MathCAD.

RECOMMENDATIONS

The overall permeability in the pure gas and mixture had been justified. For the data gathered form many sources, there were only three mechanisms; Knudsen permeability, surface permeability and viscous permeability involve in predicting the permeability of the gas species. For the next research, it is recommended to include the last mechanism which is capillary condensation that will results to more accurate prediction.

The model of the process design for this research is only on the complete mixing model. There are a few more models that can be analyzed which are cross model, countercurrent model and as well as co current flow. All the models behave in different ways and will give a different product impurity operating at different temperature and pressure. It is recommended for the next research to further study on different model to analyze the product purity and also suggested on what condition to use the model.

For this research, only first stage model is considered. More complicated when using more than one stage, and it is recommended to proceed for the next research using more than one stage. Reality, natural gas contents of more than one impurity. Somehow, this research only considered binary mixtures of moisture and methane. In order to find out more accurate prediction of the capability of the membrane for the gas separation for natural gas, it is recommended for the next study to consider the impurities contain in natural gas.

The validity of this project cannot be predicted until the experiment at the laboratory is carried out and compared it to the process modeling. For the improving and strong justification of the validity, it is recommended to have an experimental as well to compare the results with the simulation.

REFERENCE

1) R.D.Noble and S.A.Stern. 1999, "Membrane separations technology principles and applications," Membrane Science and Technology Series 2, Elsevier.

2) Nur Zurainun Zailani, 2003, " Separation of Hydrogen Sulfide using membrane technology", University Technology Petronas .

3) Yoshihiton Osada and Tsuomu Nakagawa. 1992, "Membrane science and technology, "Dekker.

4) Mohd Roslee Othman. August 2001, Kajian pemisahan gas pada membran tak organik terubahsuai, Ph.D. Thesis, Universiti Sains Malaysia, Malaysia.

5) J.D.Seader/Ernest J.Henley, 1998, Separation Process Principle, John Wiley & Sons, Inc, Chapter 14.

6) B.D. Freeman and I.Pinnau. 1999, Polymer Membranes for Gas and Vapor Separation; Chemistry and Material Science, Freeman & Pinnau.

7) S.P.nunes and K-V.Peineman. 2001, Membrane Technology in the Chemical Industry, Wiley_VCH.

8) Christie J.Geankoplis. 1993, "Transport Process and Unit Operations", 3rd Edition, Pg 462-468 and 754-757.

9) Coulson & Richardson, 1991, "Chemical Engineering", Volume 2, Particle Technology & Separation Process, Pg 745-813.

10) Robert H. Perry, Don.W.Green; Perry's Chemical Engineers' Handbook, Seventh Edition, 1997, Mc Graw Hill.

11) Michael J.Moran, Howard N.Shapiro, Fundamentals of Engineering Thermodynamic; 4th Edition; 2000, Willey.

12) Jack Winnick; Chemical Engineering Thermodynamics; 1997, Wiley.

13) Richardson M. Felder, Ronald W. Rousseau; 2000, "Elementary Principles of Chemical Process", John Willey & Sons, Inc, Thrid Edition, Pg 631 and 634

14) Brian L. Bischoff. September 2002, "Inorganic membrane technology laboratory," Oak Ridge National Laboratory <http://www.inorganicmembranes.info/uses.html>

15) William B. Durham, 1999, "Methane Hydrate", Science and Technology Review 1999, <http://www.llnl.gov/str/Durham.html.>

APPENDIX 1

Table A1: Individual Milestone for Final Research Project (FYP) January 2004

No.	Details / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Finalize the topic selection	■													
2	Familiarize with the project:		■												
	i. 1st meeting with supervisor														
	ii. Understand the project title														
	iii. Start a pre-research														
3	Preliminary Research:			■	■										
	i. Do research from internet,														
	reference book, on-line journal														
	ii. Collect all relevant data														
	iii. Start the preliminary report														
	iv. 2nd meeting with supervisor														
4	Submission the preliminary report				•										
	i. 3rd meeting with supervisor														
5	Familiarization of MathCAD:				■	■									
	i. Formulating program code														
	ii. Testing program														
	iii. 4th meeting with supervisor														
6	Start the modeling (MathCAD):						■	■							
	i. Start the progress report														
	ii. 5th and 6th meeting with supervisor														
7	Submission of progress report								•						
	i. 7th meeting with supervisor														
8	Continue project work:								■	■	■	■			
	i. 8th, 9th and 10th meeting														
	with supervisor														
	ii. Start with the dissertation final draft														
9	Submission the final draft:												•		
	i. 11th meeting with supervisor														
10	Oral presentation													•	
11	Submission of Project Dissertation														•

APPENDIX 2

Table A2: Atomic Diffusion Volumes for Use with the Fuller, Schettler and Giddings Method (Nur, 2003)

Atomic and Structural Diffusion Volume Increments, v			
C	16.5	Cl	19.5
H	1.98	S	17.0
O	5.48	Aromatic Rings	-20.2
N	5.69	Heterocyclic Ring	-20.2
Diffusion Volumes for Simple Molecules, Σv			
H_2	7.07	CO	18.9
D_2	6.70	CO_2	26.9
He	2.88	N_2O	35.9
N_2	17.9	NH_3	14.9
O_2	16.6	H_2O	12.7
Air	20.1	CCL_2F_2	114.8
Ar	16.1	SF_6	69.7
Kr	22.8	Cl_2	37.7
Xe	37.9	BR_2	67.2
Ne	5.59	SO_2	41.1

APPENDIX 3

Attachment of Natural Gas Specifications from GPP

Acquired on	:	25/02/04 09:47:57
Analysis Method	:	NGA1.M
Sample Name	:	GAS
Source	:	FEED GPP56
Data collected from	:	HP/AC Report Generator

Cal nr	Name	Ret.time	Area	Un Mol%	Mol%	Wt%
7	Nitrogen	16.948	954	0.05	0.0441	0.0609
5	Carbon dioxide	12.443	7135	6.49	5.7131	12.3837
10	Methane	18.065	71676	94.43	83.0964	65.6468
20	Ethane	14.229	7454	6.84	6.0176	8.9121
30	Propane	3.884	2399	3.54	3.1109	6.7570
43	i-Butane	4.543	1408	1.04	0.9153	2.6202
40	n-Butane	5.116	991	0.65	0.5729	1.6399
51	i-Pentane	7.078	520	0.29	0.2565	0.9114
50	n-Pentane	7.957	280	0.15	0.1327	0.4716
60	C6+	1.695	666	0.16	0.1405	0.5964
Total				113.64	100.0000	100.0000

Real Superior Cal Value (vol)	:	41.00 MJ/SM3
Real Density of Gas	:	0.8614 kg/sm3
Real Relative Density of Gas	:	0.7029
Molar Weight of Mixture	:	20.3036 g/mol
Compressibility of mixture	:	0.9970

APPENDIX 4

Sample Programming using MathCAD

)IFFERS IN PORE SIZE - DEHYDRATION NG

alculating compresibilty factor ,z

$T := 350$ $P := 60$

from perry's handbook,

$Tc := 190.6$ $Pc := 46$

$Tr := \frac{T}{Tc}$ $Tr = 1.836$ $Pr := \frac{P}{Pc}$ $Pr = 1.304$

$Bo := 0.083 - \frac{0.422}{Tr^{1.6}}$ $Bo = -0.077$ $B1 := 0.139 - \frac{0.172}{Tr^{4.2}}$ $B1 = 0.126$

$Br := Bo + 0.007 \cdot B1$ $Br = -0.076$

$z := 1 + Br \cdot \frac{Pr}{Tr}$ $z = 0.946$

Pore size range

from perry's handbook (pg 2-313), μ at T = 350 K and P = 60 bar;

$\mu := 0.0000013846$ $x := 1, 2 .. 19$

$m_{0,0} :=$ "Pore Size" $m_{3,0} := 0.4$

$m_{1,0} := 0.2$ $m_{4,0} := 0.5$ $m_{6,0} := 0.7$ $m_{9,0} := 1$

$m_{2,0} := 0.3$ $m_{5,0} := 0.6$ $m_{7,0} := 0.8$ $m_{10,0} := 1.1$ $m_{13,0} := 1.4$ $m_{16,0} := 1.7$

$m_{8,0} := 0.9$ $m_{11,0} := 1.2$ $m_{14,0} := 1.5$ $m_{17,0} := 1.8$

$m_{12,0} := 1.3$ $m_{15,0} := 1.6$ $m_{18,0} := 1.9$

$m_{19,0} := 2$

$n =$

	0
0	"Pore Size"
1	0.2
2	0.3
3	0.4
4	0.5
5	0.6
6	0.7
7	0.8
8	0.9
9	1
10	1.1
11	1.2

12	1.3
13	1.4
14	1.5
15	1.6
16	1.7
17	1.8
18	1.9
19	2

$$rp_x := m_{(x,0)} \cdot 10^{-9}$$

Viscous diffusivity

$$AVE := \frac{\left(P \cdot 10^5 + 10^5\right)}{2} \qquad AVE = 3.05 \times 10^6$$

$$viscous_x := AVE \cdot \frac{\left(rp_x\right)^2}{8 \cdot \mu}$$

$viscous_x =$

$1.101 \cdot 10^{-8}$
$2.478 \cdot 10^{-8}$
$4.406 \cdot 10^{-8}$
$6.884 \cdot 10^{-8}$
$9.913 \cdot 10^{-8}$
$1.349 \cdot 10^{-7}$
$1.762 \cdot 10^{-7}$
$2.23 \cdot 10^{-7}$
$2.754 \cdot 10^{-7}$
$3.332 \cdot 10^{-7}$
$3.965 \cdot 10^{-7}$
$4.653 \cdot 10^{-7}$
$5.397 \cdot 10^{-7}$
$6.195 \cdot 10^{-7}$
$7.049 \cdot 10^{-7}$
$7.958 \cdot 10^{-7}$
$8.921 \cdot 10^{-7}$
$9.94 \cdot 10^{-7}$

Knudsen Diffusivity

$$knudsen_x := \frac{2}{3} \cdot \left(rp_x - 1.9 \cdot 10^{-10}\right) \cdot \sqrt{8.8314 \cdot \frac{T}{\pi \cdot 16}}$$

$knudsen_x =$

$5.228 \cdot 10^{-11}$
$5.751 \cdot 10^{-10}$
$1.098 \cdot 10^{-9}$
$1.621 \cdot 10^{-9}$
$2.143 \cdot 10^{-9}$
$2.666 \cdot 10^{-9}$
$3.189 \cdot 10^{-9}$
$3.712 \cdot 10^{-9}$
$4.235 \cdot 10^{-9}$
$4.757 \cdot 10^{-9}$
$5.28 \cdot 10^{-9}$
$5.803 \cdot 10^{-9}$
$6.326 \cdot 10^{-9}$
$6.848 \cdot 10^{-9}$
$7.371 \cdot 10^{-9}$
$7.894 \cdot 10^{-9}$
$8.417 \cdot 10^{-9}$
$8.94 \cdot 10^{-9}$
$9.462 \cdot 10^{-9}$

$1.101 \cdot 10^{-6}$

$\Delta H := 8179$

Bulk Diffusivity

$$\text{bulk} := 10^{-7} \cdot T^{1.75} \cdot \frac{\left(\frac{1}{16.043} + \frac{1}{18.0}\right)^{0.5}}{P \cdot \left(\sqrt[3]{24.42} + \sqrt[3]{9.44}\right)^2}$$

$\text{bulk} = 6.445 \times 10^{-7}$

surface diffusivity

$$\text{surface} := 0.016 \cdot 0.0001\, e^{-0.45 \cdot \frac{\Delta H}{8.314 \cdot T}}$$

$\text{surface} = 4.517 \times 10^{-7}$

Permeability Factor

$\varepsilon := 0.272 \qquad \tau := 3.676$

$$\text{Factor} := \frac{\varepsilon}{z \cdot 8.314 \cdot \tau \cdot T} \qquad \text{Factor} = 2.687 \times 10^{-5}$$

gas diffusion (m2/s)

$$\text{GasDiff}_x := \frac{1}{\frac{1}{\text{knudsen}_x} + \frac{1}{\text{bulk}}}$$

$\text{GasDiff}_x =$

$5.227 \cdot 10^{-11}$
$5.746 \cdot 10^{-10}$
$1.096 \cdot 10^{-9}$
$1.617 \cdot 10^{-9}$
$2.136 \cdot 10^{-9}$
$2.655 \cdot 10^{-9}$
$3.173 \cdot 10^{-9}$
$3.691 \cdot 10^{-9}$
$4.207 \cdot 10^{-9}$
$4.722 \cdot 10^{-9}$
$5.237 \cdot 10^{-9}$

Viscousity Permeability

$\text{vp}_x := \text{Factor} \cdot \text{viscous}_x$

$\text{vp}_x =$

$2.96 \cdot 10^{-13}$
$6.66 \cdot 10^{-13}$
$1.184 \cdot 10^{-12}$
$1.85 \cdot 10^{-12}$
$2.664 \cdot 10^{-12}$
$3.626 \cdot 10^{-12}$
$4.736 \cdot 10^{-12}$
$5.994 \cdot 10^{-12}$
$7.4 \cdot 10^{-12}$
$8.953 \cdot 10^{-12}$
$1.066 \cdot 10^{-11}$

Knudsen Permeability

$\text{kp}_x := \text{Factor} \cdot \text{GasDiff}_x$

$\text{kp}_x =$

$1.405 \cdot 10^{-15}$
$1.544 \cdot 10^{-14}$
$2.945 \cdot 10^{-14}$
$4.344 \cdot 10^{-14}$
$5.741 \cdot 10^{-14}$
$7.135 \cdot 10^{-14}$
$8.528 \cdot 10^{-14}$
$9.918 \cdot 10^{-14}$
$1.131 \cdot 10^{-13}$
$1.269 \cdot 10^{-13}$
$1.407 \cdot 10^{-13}$
$1.546 \cdot 10^{-13}$

5.751·10 -9
6.264·10 -9
6.776·10 -9
7.288·10 -9
7.799·10 -9

1.251·10 -11
1.45·10 -11
1.665·10 -11
1.894·10 -11
2.138·10 -11
2.397·10 -11
2.671·10 -11
2.96·10 -11

1.683·10 -13
1.821·10 -13
1.959·10 -13
2.096·10 -13
2.233·10 -13
2.37·10 -13
2.506·10 -13

Surface Permeability

$$sp_x := Factor\cdot surface\cdot\frac{1}{\varepsilon}\cdot 1140\cdot 215\cdot 10^{-7}\cdot 6\cdot\frac{10^{-9}}{rp_x}$$

$sp_x =$

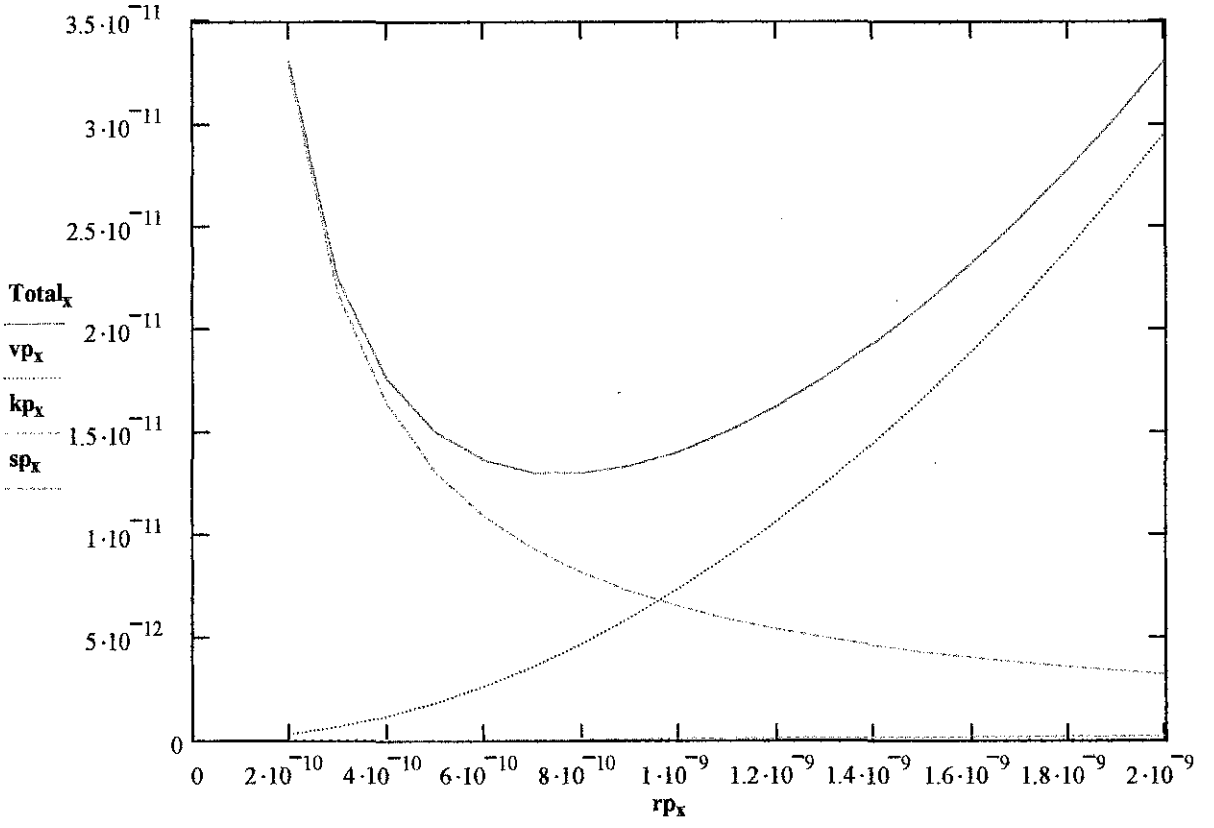
3.281·10 -11
2.187·10 -11
1.641·10 -11
1.312·10 -11
1.094·10 -11
9.375·10 -12
8.203·10 -12
7.291·10 -12
6.562·10 -12
5.966·10 -12
5.469·10 -12
5.048·10 -12
4.687·10 -12
4.375·10 -12
4.101·10 -12
3.86·10 -12
3.646·10 -12
3.454·10 -12
3.281·10 -12

Total Permeability

$$Total_x := vp_x + kp_x + sp_x$$

$Total_x =$

3.311·10 -11
2.256·10 -11
1.762·10 -11
1.502·10 -11
1.366·10 -11
1.307·10 -11
1.302·10 -11
1.338·10 -11
1.407·10 -11
1.505·10 -11
1.626·10 -11
1.771·10 -11
1.936·10 -11
2.121·10 -11
2.324·10 -11
2.545·10 -11
2.784·10 -11
3.04·10 -11
3.313·10 -11



$Total_x$: Total Permeability

vp_x : Viscous Permeability

sp_x : Surface Permeability

kp_x : Knudsen Permeability